

POLYCHLORINATED DIBENZOFURAN (PCDF) PREDICTION FROM DIBENZOFURAN CHLORINATION

Jae-Yong Ryu,¹ James A. Mulholland,¹ and James E. Dunn²

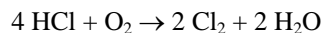
¹ Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0512, USA

² Department of Mathematical Sciences, University of Arkansas, Fayetteville, AR 72701, USA

Introduction

In municipal waste incinerators, chlorination of dibenzofuran (DF) may be a significant source of polychlorinated dibenzofurans (PCDFs), particularly less chlorinated congeners, due to the high concentration of unsubstituted phenol in the flue gas.¹ At temperatures between 600 and 800°C, condensation of phenol readily produces DF. Often DF and the less chlorinated PCDFs are not measured, however, due to their lower toxicity relative to the 2,3,7,8 congeners. Wikstrom and Marklund¹ found the concentration of DF in incineration exhaust gas to be greater than the total PCDF concentration by a factor of 100 to 1000, and speculated that the source of PCDFs was the chlorination of DF on particle surfaces at low temperatures.

Dibenzofuran chlorination can occur by metal catalysis, and, in particular, by copper (II) chloride (CuCl₂). The Deacon process can convert HCl to Cl₂, which then can lead to gas-phase DF chlorination. The overall Deacon reaction is as follows.



Alternatively, direct chlorination of an aromatic molecule such as DF by CuCl₂ can occur by the following overall transfer process.^{2,3}



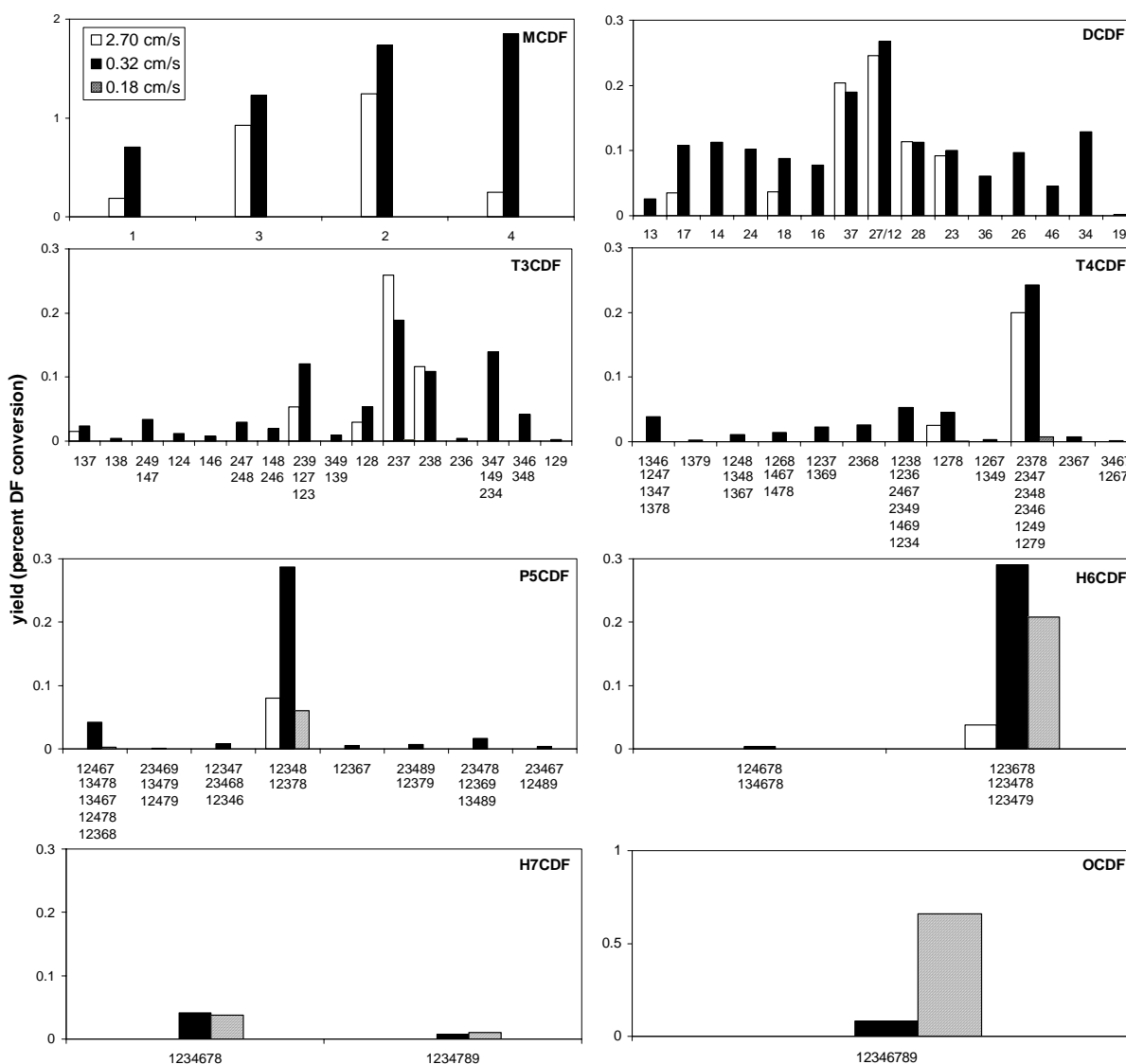
Isomer distribution patterns can be used as a fingerprint of formation mechanism. Patterns from DF chlorination have already been explained in detail.⁴ Favored formation of 2,3,7,8 congeners was observed. In this paper, distributions of PCDF products formed by CuCl₂-catalyzed chlorination of DF at three different gas velocities over a range of temperatures are used to develop a probabilistic model for PCDF formation by this mechanism.

Methods and Materials

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. High purity DF reactant (40 mg) was placed in a glass vessel and heated. DF vapor was transported to the reactor by a gas stream of nitrogen with 8% oxygen. The resulting gas stream contained 0.1% DF vapor (nominal). A particle bed consisting of 1 g silicon dioxide (SiO₂) with CuCl₂ (0.5% Cu, mass) was located at the center of the reactor. The SiO₂/CuCl₂ particle bed was prepared by mechanical mixing. Preliminary experiments performed with only SiO₂ confirmed its inertness under these conditions. The thermal stability of CuCl₂ in the flow reactor was assessed by performing experiments with a gas stream without organic vapor. CuCl₂ recoveries of greater than 95% were observed at temperatures of 400°C and less. Soluble product gases were collected in a dichloromethane trap and analyzed by GC/MS. More detailed descriptions of experimental and analytical conditions are presented elsewhere.⁴

Results and Discussion

PCDF product yields for experiments at 300°C and gas velocities of 2.7, 0.32 and 0.18 cm/s are shown in Figure 1. Total conversion of DF to PCDF products ranged from 1 to 8%. At high gas velocity, the degree of chlorination was least. At low gas velocity, although the total conversion of DF to PCDFs was lowest, the degree of chlorination was highest. The intermediate gas velocity produced the broadest distribution of PCDF products. In all cases, the major T₄CDF, P₅CDF, and H₆CDF products were the 2,3,7,8 substituted congeners, the favored chlorination sites for DF. Differences in isomer patterns were



observed, however.

Figure 1. PCDF product yields from DF chlorination at 300°C at gas velocities of 2.7, 0.32 and 0.18 cm/s.

In particular, more products with 4,6 Cl substituents were observed at low gas velocity and high gas temperature (not shown). We attribute this result to the greater stability of these congeners.

Iino and coworkers^{5,6} observed these congeners as favored in dechlorination of OCDF. Iino and coworkers^{5,6} developed a first-order statistical model for predicting PCDF product distributions from OCDF dechlorination, based on the experimentally observed H₇CDF isomer distribution. Here, we develop a similar model for predicting PCDF product distributions from DF chlorination, based on the experimentally observed MCDF isomer distribution. Our conditional probability modeling approach is an improvement over Iino's modeling approach in that it accounts for the depletion of sites as reaction proceeds. Both models are limited to the case in which the destruction of PCDF products is negligible compared to the formation of PCDF products.

We describe our model using the example of 1,2,3-T₃CDF. Let F_{1,2,3} be the isomer fraction of 1,2,3-T₃CDF produced by DF chlorination, P(1,2,3) be the probability of chlorinating the 1,2,3 positions of DF, and S_{1,2,3} be the statistical factor related inversely to molecular symmetry. The isomer fraction is calculated as follows.

$$(1) F_{1,2,3} = S_{1,2,3} P(1,2,3)$$

For 1,2,3-T₃CDF, the statistical factor is 2 because there are two sets of sites on DF that can be chlorinated to produce 1,2,3-T₃CDF. The probability of chlorinating one of the sets of sites is calculated by summing the probabilities for all orders of chlorination, as follows.

$$(2) P(1,2,3) = P(\underline{1,2,3}) + P(\underline{1,3,2}) + P(\underline{2,1,3}) + P(\underline{2,3,1}) + P(\underline{3,1,2}) + P(\underline{3,2,1})$$

Here, P(1,2,3) is the probability of chlorinating first the 1 site of DF, then the 2 site, and then the 3 site. In general, this equation will have n factorial terms, where n is the number of chlorines in the PCDF product. The probability of chlorination proceeding in a specific order is given as follows.

$$(3) P(\underline{1,2,3}) = P(1) P(2 | 1) P(3 | 1, 2)$$

Here, P(1) is the probability of DF chlorination at position 1, P(2 | 1) is the probability of chlorination at position 2 given position 1 is already chlorinated, and P(3 | 1, 2) is the probability of chlorination at position 3 given positions 1 and 2 are already chlorinated.

An assumption in our first-order model is that the probabilities of chlorinating dibenzofuran sites 1 and 9, 2 and 8, 3 and 7, and 4 and 6 are the same, regardless of chlorine substitution. These are obtained from the distribution of MCDF isomers. From the high gas velocity experiment we obtain the following: P(1) = P(9) = 0.03; P(2) = P(8) = 0.19; P(3) = P(7) = 0.27; P(4) = P(6) = 0.01. The sum of probabilities for chlorinating one of the eight possible sites on DF is one; thus, there are three experimentally-derived independent parameters used thus far in the model. We introduce a fourth parameter to account for a second-order effect – the steric hindrance associated with having both bay sites (1,9) chlorinated in the PCDF product. From the experimental data, we observe that the probability of chlorinating a second bay site is 90% less than that for chlorinating the first bay site. For example, P(9 | 1) = P(9)*0.1 = 0.003. Thus, we use four experimentally-derived parameters in our model.

Predicted and measured PCDF isomer fractions are shown in Figure 2 for all experimental results. In the case of the 2.7 cm/s isomer fractions, the average and standard deviation of measurements at five temperatures between 200 and 300°C are shown. Qualitatively, the model predicts the major isomers, those containing 2,3,7,8 substituents, and the order of isomer yields well. As expected, discrepancies between observation and prediction were greatest for MCDF, DCDF, and T₃CDF isomers from the low gas velocity experiment in which destruction of these isomers was significant. For more quantitative prediction of isomer patterns, a more mechanistic model is needed to account for effects of chlorine substitution and subsequent chlorination and effects of reaction conditions and PCDF destruction.

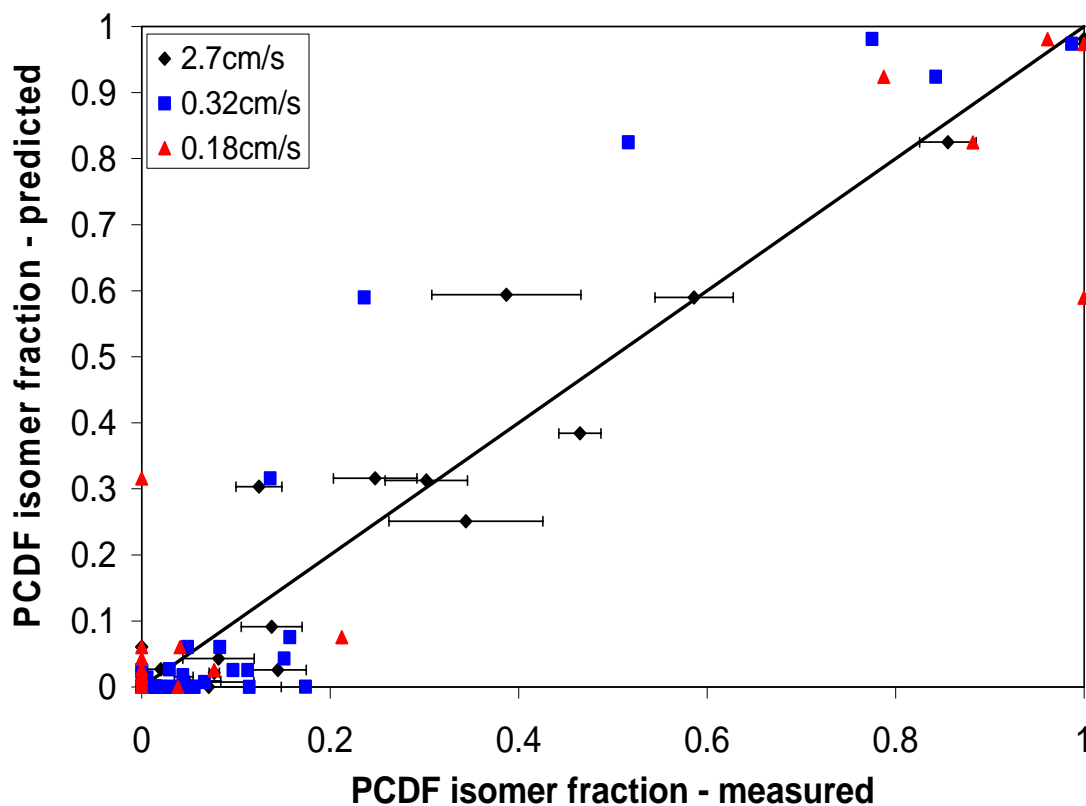


Figure 2. Measured and computed PCDF isomer fractions from DF chlorination.

The simplicity of the statistical model presented makes it a useful approach for estimating PCDF isomer patterns that can be used as a diagnostic of formation by DF chlorination. The results demonstrate the potential role of DF chlorination in the formation of toxic PCDF congeners.

Acknowledgement

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